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A NEW CONCEPTION OF THERMAL PRESSURE AND A THEORY OF SOLUTIONS.

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Introduction.

For an understanding of all kinds of physico-chemical equilibrium a further insight is necessary into the nature of the conditions which exist in the interior of any homogeneous phase. It will be the aim of the present paper to study this problem in the light of a new theory, which, although opposed to some ideas which are now accepted as correct, yet recommends itself by its simplicity and by its ability to explain several important phenomena which have hitherto received no satisfactory explanation.

The theory suggested itself in the consideration of certain remarkable general laws which treat of heterogeneous equilibrium in which the several phases are subject to different pressures. These laws will be discussed in the first section of this paper, and in the second section it will be shown that they can all be explained by a single simple assumption. In the third section it will be shown that the same assumption is alone sufficient to explain all the laws of dilute solutions. In the last section other consequences of the new theory will be discussed, especially in their relation to the theory of van der Waals.

I.

The Effect of Pressure on the Tendency to Pass from Phase to Phase.

It has been shown by several investigators * that, in a number of cases of heterogeneous equilibrium, if the pressure upon one of the phases alone is changed, a readjustment takes place that can be easily calculated.

* Poynting, Phil. Mag. (5), XII. 32 (1881); Schiller, Wied. Ann., LIII. 396, (1894); Hall, Jour. of Phys. Chem., III. 452 (1899.)

In order to introduce a general discussion of this problem, which leads to very notable and instructive results, let us consider first a simple, special case, namely, the question of the effect upon the vapor pressure of a liquid caused by a change in the total pressure on the surface of the liquid.

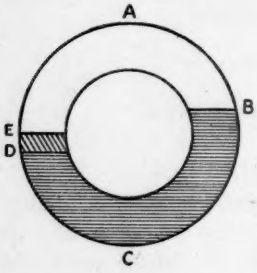

FIGURE 1.

Figure 1 represents a ring-shaped enclosure containing a liquid X in the part B C D, and the vapor of X throughout the remaining space. The space D E contains also an infinitesimal layer of some inert and insoluble gas, which is prevented from diffusing into the space B A E by a membrane at E, which is permeable only to the vapor of X. The foreign gas thus enclosed exerts a pressure upon the liquid at D and maintains a difference of level, $d\,H$, between B and D*. This pressure, moreover, must have an effect upon the vapor pressure of the liquid, for, on account of its weight, the pressure of the vapor is greater at D than at B, but the liquid is in equilibrium with the vapor at both points, therefore the vapor pressure of the liquid is greater at D than at B. If $d\,P_1$ represent the difference in vapor pressure between B and D, and s_1 the specific gravity of the vapor, then we may write,

$$d\,P_1 = s_1\,d\,H.$$

If $d\,P_2$ represent the difference in the total pressure upon the liquid at B and D, and s_2 the specific gravity of the liquid, then

$$d\,P_2 = s_2\,d\,H.$$

From these two equations,

$$\frac{d\,P_1}{d\,P_2} = \frac{s_1}{s_2},$$

or if σ_1 and σ_2 represent the specific volumes of vapor and liquid respectively, then

$$\frac{d\,P_1}{d\,P_2} = \frac{\sigma_2}{\sigma_1}. \qquad (1)$$

* Objection has been raised to proofs of this kind; thus, in this case, it would be argued that in reality the liquid will distil from B to the space above E. That this may happen in no way invalidates the proof, for it is not necessary that it should happen. By keeping E A free from drops of the liquid the system is in perfect equilibrium, the equilibrium of supersaturation. That there is another more stable equilibrium possible is of no concern.

In general, therefore, an increase in the total pressure upon a liquid will cause an increase in the vapor pressure, and the ratio of the two changes will be the ratio of the specific gravities of liquid and vapor. This relation, which has been stated before in several different forms, has an importance which has been hitherto overlooked, probably because, under ordinary circumstances, the calculated effect upon the vapor pressure has been too small to be measurable, and also because the result has usually been obtained by assuming the applicability of the gas law to the vapor, thus making the result seem only an approximation.

Although ordinarily the magnitude of the effect is extremely small, in some cases it must be of considerable significance. Equation (1) shows that the influence of external pressure upon the vapor pressure depends upon the relative densities of vapor and liquid. Therefore, for liquids of high molecular weight, as a rule, the effect will be considerable, and also in the case of a liquid whose vapor is under high pressure. But especially must the effect be considered in the study of critical phenomena and the influence of foreign substances in the determination of the critical constants, for in the region about the critical point the densities of liquid and vapor approach identity. The proof of equation (1) given above shows that its validity rests upon no assumption as to the specific nature of the two phases considered. The probability is immediately suggested that equation (1) is simply a special statement of a general law applying to all heterogeneous equilibrium. That this is true may be shown in the following way.

In figure 2, let A B C and A′ B′ C′ represent two similar enclosures. In the first, X_1 and X_2 are two different phases of a simple substance X; P_1 and P_2 are the pressures exerted by an inert gas on the two sides and are such that equilibrium exists; B is a membrane permeable only to the vapor of X. The specific volumes in phases X_1 and X_2 are σ_1 and σ_2 respectively. The enclosure A′ B′ C′ is the same as A B C except that here there is another state of equilibrium in which the pressures upon the phases X_1 and X_2 are $P_1 + dP_1$ and $P_2 + dP_2$, and the specific volumes are $\sigma_1 - d\sigma_1$ and $\sigma_2 - d\sigma_2$ respectively.

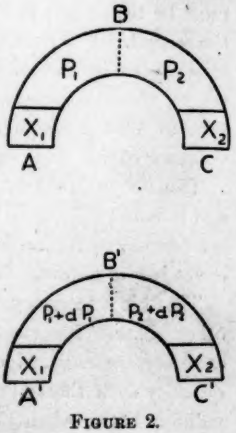

FIGURE 2.

Now let the following process occur reversibly and isothermally: (1) One gram of X_1 is

removed from A at pressure P_1; (2) it is compressed to $P_1 + dP_1$; (3) it is introduced into the second enclosure at A′ against pressure $P_1 + dP_1$; (4) one gram of X_2 is taken from the second enclosure at C′ at pressure $P_2 + dP_2$; (5) it is allowed to expand to P_2; (6) it is introduced into the first enclosure at C against pressure P_2.

The system will have returned now by internal adjustment to its original condition. The quantities of work done by the system in the several steps are,

$$W_1 = P_1 \sigma_1,$$
$$W_2 = - P_1 d\sigma_1,$$
$$W_3 = - (P_1 + dP_1)(\sigma_1 - d\sigma_1),$$
$$W_4 = (P_2 + dP_2)(\sigma_2 - d\sigma_2),$$
$$W_5 = P_2 d\sigma_2,$$
$$W_6 = - P_2 \sigma_2.$$

By writing the sum of these terms equal to zero, according to the second law of thermodynamics, we obtain the equation,

$$\sigma_2 dP_2 - \sigma_1 dP_1 = 0; \quad \text{or,} \quad \frac{dP_2}{dP_1} = \frac{\sigma_1}{\sigma_2}. \tag{2}$$

The meaning of this equation is obvious. When under any conditions two phases of a substance are in equilibrium and the pressure is increased upon one phase, then in order to maintain equilibrium the pressure must be increased on the second phase; and the second change in pressure must be to the first as the specific volume of the first phase is to that of the second. For example, if ice and water are in equilibrium at atmospheric pressure and an additional pressure of one atmosphere is put upon the ice alone, then equilibrium can be maintained by an additional pressure of 1.09 atmospheres upon the water, since 1.09 is the ratio of the volumes of ice and water.

The above law has been derived without any assumption whatever, and is based only upon the second law of thermodynamics. It must be considered, therefore, in the same degree as the latter a universal and exact law of nature. This law may be presented in another form.

There is a tendency for the particles of every phase to escape into some other phase. Later a function ψ will be so defined as to represent this *escaping tendency*. Here it will be sufficient to consider ψ merely a quantity such that when two phases are in equilibrium, ψ has the same value in both; when not in equilibrium, ψ is greater in the less stable

phase. When two phases in equilibrium are subjected to infinitesimal changes of pressure resulting in a second state of equilibrium,

$$d\psi_1 = d\psi_2, \text{ or in other terms, } \frac{\partial \psi_1}{\partial P_1} dP_1 = \frac{\partial \psi_2}{\partial P_2} dP_2,$$

where ∂ denotes a partial differential; finally,

$$\frac{\frac{\partial \psi_1}{\partial P_1}}{\frac{\partial \psi_2}{\partial P_2}} = \frac{dP_2}{dP_1} = \frac{\sigma_1}{\sigma_2},$$

from equation (2). In general, therefore,

$$\frac{\partial \psi}{\partial P} = \kappa \sigma, \tag{3}$$

where κ is a constant.

That is, *the change in the escaping tendency of any phase with a given change in the external pressure is proportional to the specific volume of the phase.* For example, if solid and liquid benzol are in equilibrium at one pressure and this pressure is increased, the escaping tendency of the liquid is increased more than that of the solid in the ratio of the specific volumes, 1.13 to 1.11. The liquid phase, therefore, totally disappears. In the case of water, whose liquid is denser than the solid, the phenomenon is exactly reversed. The above law, therefore, expresses quantitatively what the principle of Le Chatelier states qualitatively.

In the preceding discussions we have dealt with different phases of a simple substance, not with a mixture, but the same method of proof and therefore the same law can be shown to be applicable to all cases in which the phases considered are all capable of being converted entirely, under the conditions of equilibrium which exist,* into one substance, whether this be a pure substance or a mixture.

Equations (1), (2), and (3) apply, therefore, to all cases where there is association, dissociation, polymerization, or isomerization, provided that all these different molecular species are in "true" equilibrium with one another.

* This qualifying phrase is necessary. The different phases must not merely have the same composition. Thus, a system composed of water and a gaseous phase of hydrogen and oxygen in equivalent proportions differs essentially from a system of solid ammonic sulphydrate and a gaseous phase containing ammonia and hydrogen sulphide in equivalent proportions. The latter is subject to the above treatment, the former is not.

For the sake of completeness the corresponding phenomena in the case of other mixtures will next be considered.

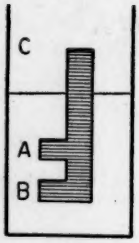

FIGURE 3.

In Figure 3 let the tube C A B contain a homogeneous mixture of liquids and the outer vessel one of the pure liquids, X, alone. A and B represent two membranes permeable to X alone. If pressure is applied in the tube so that X neither enters nor leaves the tube at A, then there will be equilibrium at B also, for otherwise a continuous cyclic process would be kept up, contrary to the second law of thermodynamics. The escaping tendency of X is the same outside and inside at A and also at B, since there is equilibrium at both points, but the changes in pressure between A and B which determine the magnitude of that tendency are different inside and outside the tube. If dH is the height A B, and the specific gravity of the mixture and the liquid X are S_1 and S_2 respectively, the changes in pressure are $S_1 dH$ inside the tube and $S_2 dH$ outside. If dP_1 and dP_2, respectively, represent these changes in pressure,

$$\frac{dP_1}{dP_2} = \frac{S_1}{S_2}; \quad \text{or} \quad \frac{dP_1}{dP_2} = \frac{\sigma_2}{\sigma_1}.$$

This is the same as equation (2), and at first sight it seems that the influence of pressure upon the equilibrium between two phases is as simple in the case of mixtures as in the case of pure substances. It is actually, however, much more complicated. In the above example there is a change in the escaping tendency of X from the mixture, not only because there is a change of pressure, but also because, in general, between A and B there is a change in the relative amounts of the components of the mixture. In other words, the concentration of X differs at A and B.* Moreover if there is chemical equilibrium in the mixture the chemical reaction will have run nearer to completion in A or in B according to whether the total volume is increased or diminished by the reaction. On account of this complexity the further study of mixtures, although of much interest, must be deferred, since it is not essential to the present paper.

* See Gouy and Chaperon, Ann. Ch. Ph. (6), XII. 384 (1887).

II.

Thermal Pressure.

When we consider again the laws which govern different phases of a simple substance, as expressed in equations (1), (2), and (3), their great simplicity and generality suggest that some equally simple physical explanation is possible. As we have already seen, an increase in the external pressure always produces an increase in the tendency of a substance to escape from any phase. The pressure can influence this tendency only by changing the conditions within the phase. Let us briefly analyze these conditions.

If in the interior of any homogeneous phase of infinite extent, not subject to gravity, we imagine a septum of infinitesimal thickness, i. e. a mathematical plane, there is every reason to believe that upon each side of this septum there would be a pressure exerted which would depend upon the temperature, and would in general differ from the pressure observed at the surface of the phase. This internal pressure will be termed the *thermal pressure* of the phase. It would be expressed, in the hypothetical terms of the kinetic theory, as equal to the number of molecules passing from one side to the other in unit time through an imaginary plane of unit area, multiplied by twice the average momentum of each molecule in the direction perpendicular to the plane.

An illustration of the meaning of thermal pressure is the quantity $\frac{RT}{v-b}$ in the equation of van der Waals; this quantity, if the theory of van der Waals is correct, represents the thermal pressure of a compressed gas. Thermal pressure will denote the pressure due to heat in distinction from that due to attractive or repulsive forces.

The actual pressure observed at the surface of the phase may be considered equal to the thermal pressure plus or minus the resultant of all other repulsive or attractive forces acting in the phase. This resultant will be called the *attractive pressure* and designated by a, — positive if an attractive force, negative if repulsive. If the thermal pressure is represented by β we have the equation,

$$\beta - a = P, \tag{4}$$

where P is the external pressure. This equation combined with equation (3) gives,

$$\frac{d\psi}{d(\beta - a)} = \kappa\sigma, \tag{5}$$

that is, the tendency of a substance to escape from a phase is greater, the greater the thermal pressure and the less the attractive pressure. Now equation (5) applies to any phase of any pure substance, solid, liquid, or gaseous. In some cases a small change in pressure will cause a very great change in both β and α; in others, a very small change in both. The change in β relative to that in α will sometimes be very great, sometimes very small. In general, the function ψ depends, not upon the absolute, individual magnitudes of β and α, but only upon their difference; and we may conclude from the very universality of equation (5) that it is true not merely when β and α are changed by a change in the external pressure, but that in general a change in β or α, no matter how caused, will affect the quantity ψ only as it changes their difference $\beta - \alpha$, and that any change in β accompanied by an equal change in α has no effect on ψ since one neutralizes the other. This will be a necessary postulate in the development of the following theory.

Let us consider a system composed of a liquid or solid phase and its vapor, under such circumstances that the latter obeys the laws of a perfect gas. By equation (1), if we replace $\frac{\sigma_2}{\sigma_1}$ by $\frac{v_2}{v_1}$, the molecular volumes, and write $v_1 = \frac{RT}{P_1}$ where R is the gas constant, T the absolute temperature, we obtain

$$\frac{dP_1}{dP_2} = \frac{v_2}{v_1}; \text{ or, } \frac{dP_1}{dP_2} = \frac{P_1 v_2}{RT}; \text{ or, } \frac{dP_1}{P_1} = \frac{dP_2}{\left(\frac{RT}{v_2}\right)}. \qquad (6)$$

This equation expresses the very remarkable result that the change in vapor pressure is to the total vapor pressure as the change in the external pressure upon the solid or liquid phase is to the pressure which that phase would exert if it should behave as a perfect gas. This may be presented in different form by the aid of equation (4) as,

$$\frac{dP_1}{P_1} = \frac{d(\beta_2 - \alpha_2)}{\left(\frac{RT}{v_2}\right)}. \qquad (7)$$

In attempting an explanation of these relations let us consider first a case in which the change in α_2 is negligible compared with the change in β_2. That is, β_2 changes while α_2 remains constant. Since the attractive forces remain constant, it might be predicted *a priori* that the vapor pressure would be proportional to β_2, the thermal pressure, especially if the kinetic point of view is adopted; for the vapor pressure is believed to be

dependent upon the chance of any one molecule to escape from the phase in question and upon the number of molecules per second which share this chance. This chance for each molecule will depend (1) upon its momentum and (2) upon the various influences that retard its motion outward. The latter are the various attractive forces that have been included in the quantity a_2. Therefore in any isothermal change in which a_2 is constant neither the momentum * nor the retarding influences vary, and the vapor pressure then will be proportional to the number of molecules coming to the surface per second, and therefore proportional to the thermal pressure. Hence,

$$P_1 = k\beta_2; \text{ or, } \frac{dP_1}{P_1} = \frac{d\beta_2}{\beta_2}. \tag{8}$$

Moreover in the general case, when both β_2 and a_2 change, if we postulate, as on page 152, that equal changes in β_2 and a_2 produce equal and opposite effects on the vapor pressure, then we should expect that the change in vapor pressure would be to the total vapor pressure as the *effective* change in thermal pressure is to the total thermal pressure; if "effective change" in β_2 is used to mean the change in β_2 over and above that required to compensate for change in a_2. That is,

$$\frac{dP_1}{P_1} = \frac{d(\beta_2 - a_2)}{\beta_2}. \tag{9}$$

Comparing this equation, derived from kinetic considerations, with the one which has been proved thermodynamically, namely, equation (7),

$$\frac{dP_1}{P_1} = \frac{d(\beta_2 - a_2)}{\left(\frac{RT}{v_2}\right)},$$

it is evident that the only assumption necessary to make the two identical is the following: *The thermal pressure of any phase is equal to the pressure which the substance would exert if, under the same conditions, it should behave as a perfect gas.*

Objection to this assumption cannot be made on the ground that it is not sufficiently simple; but is it too simple? What has become of the correction "b" of van der Waals, to say nothing of all the complications that may exist in a liquid or solid phase? It must be confessed that the above assumption seems, at first sight, absurdly simple and quite improbable. I shall attempt to show, however, that this assumption is not only

* Whether this momentum is quite constant will be considered later.

not opposed to any facts, but is capable of explaining many facts besides those which we have already discussed. On the other hand, this assumption seems entirely irreconcilable with one of the accepted principles of the kinetic theory, but it is directly deducible from this theory if the latter is modified in the way which will now be proposed.

In the kinetic theory of gases there are two quantities of fundamental importance: one is the kinetic energy of a molecule, and is represented by $\frac{1}{2} mu^2$, where m is the mass, and u the velocity of the molecule; the other is that which has been called thermal pressure, and is proportional to $mu \times n$, the product of mu, the momentum of the molecule and n, the number of molecules whose centres of gravity pass in one second through unit area. In the perfect gas n is proportional to u; the kinetic energy and the thermal pressure in a perfect gas are proportional to each other and to mu^2. In substances, however, which deviate from the condition of a perfect gas the kinetic energy will still be proportional to mu^2, but $(mu)\, n$ will be proportional to mu^2 only when n is proportional to u, and this will be the case only when the molecules behave on collision as perfectly elastic mathematical particles, that is, when there is no correction corresponding to the quantity b of van der Waals.

In the kinetic theory of gases the temperature is shown to be measured by mu^2, and in every attempt hitherto to extend this theory to less simple conditions of matter the fundamental assumption has been that the kinetic energy of progression of the molecule is proportional to the absolute temperature. I now propose to reject this assumption entirely, and to substitute the assumption that the temperature is in all cases measured by the quantity $(mu)\, n$ or by the thermal pressure; more explicitly, instead of assuming that the kinetic energy of a molecule of any substance is the same as if it were a perfect gas, while the quantity $(mu)n$ may vary in any way, it will now be assumed that $(mu)\, n$ in any substance is the same as it would be if the substance should behave as a perfect gas and that at one temperature the average kinetic energy of progression of the molecule may vary.

This proposition appears less revolutionary if it is borne in mind that in the only case in which the kinetic theory is entirely satisfactory, namely, the perfect gas, the two assumptions become identical, and, therefore, the change in no way affects the previous kinetic explanation of all the phenomena of gases. The only other application of the kinetic theory that has met with any degree of success, the equation of van der Waals, will be discussed later in its relation to this new kinetic conception.

In the meantime it is necessary to consider what advantage in theory may be gained by adopting the proposed assumption. According as we deal with a pure substance or a mixture, the quantity $(mu)\,n$ will be a measure of the total thermal pressure, or of the partial thermal pressure of any one molecular species, if we so designate that pressure which may be conceived to be exerted on either side of an infinitesimally thick membrane in the interior of a homogeneous phase by the molecules of that particular molecular species. The principle of thermal pressure offered on page 153 may be put in the form of an equation, as,

$$\beta = \frac{n\,R\,T}{V}, \qquad (10)$$

where β is the partial or total thermal pressure, as the case may be, of some one molecular species; n is the number of gram molecules of this species; R is the gas constant; T, the absolute temperature; and V, the total volume occupied.

This idea could be otherwise expressed by an extension of the rule of Avogadro, as follows: *All substances at the same temperature and the same thermal pressure have the same number of molecules in unit volume.*

Equation (10), which, if correct, represents a universal principle of nature, must be capable of very wide application. In the next section it will be shown that by assuming the correctness of this equation, and without any other hypothesis, it is possible to derive all the laws of dilute solutions. It is well to emphasize that while equation (10) was shown to be consistent with the kinetic theory in order that it might appear more probable, still, having once assumed this equation, it is unnecessary henceforth to adopt any kinetic view whatever.

III.

A Theory of Solutions.

Notwithstanding the simplicity of the phenomena of solutions, they have as yet received no entirely adequate explanation. In fact, in some explanations assumptions have been necessary that are inherently improbable. In the theory of solutions here presented it will be unnecessary to assume either that the solute does or does not combine chemically with the solvent in any way. It will only be necessary to suppose that when n gram molecules of any substance are dissolved in a solvent, that

in the solution there are still n gram molecules of something different from the solvent itself.*

All the general laws of solutions may be derived thermodynamically from either of two empirical equations, each of which, moreover, may be derived from the other. The first is the law of van 't Hoff,

$$\Pi = \frac{n R T}{V}, \tag{11}$$

where Π is the osmotic pressure of a solution containing n gram molecules of a solute in a volume V.

The second may be written,

$$\frac{\psi_1 - \psi_2}{\psi_1} = \frac{n}{n + m}, \tag{12 a}$$

or, more strictly,

$$\frac{d\psi}{\psi} = \frac{dn}{m}. \tag{12 b}$$

In (12 a) n and m represent the number of gram molecules of solute and solvent respectively; ψ_1 and ψ_2 denote the escaping tendencies of the solvent from the pure solvent and the solution respectively; in (12 b) $d\psi$ represents the change in the escaping tendency of the solvent, due to dn gram molecules of the solute. In order to make the equations entirely definite it is necessary to give the function ψ, or the escaping tendency, a meaning less vague than that which sufficed on page 148, by defining the actual value of ψ for some one condition of each substance. Therefore the escaping tendency of a perfect gas will be defined as equal to its gas pressure, and the escaping tendency from most actual gaseous phases will be approximately the partial gas pressure.

Equation (12 b) simply unites in one general equation the law of Raoult for the lowering of vapor pressure, the law of Nernst for the lowering of solubility, and less directly the law for the depression of the

* It is probable that, in some cases, "association" with the solvent takes place and in others that it does not. A crystal containing water of crystallization seems in no way different from any other double salt, and since it has often been shown that double salts exist as such in solution, it is probable that water enters into many molecular compounds in solution. Thus it seems probable that when a salt forms a number of solid hydrates, all these compounds and others whose solubility is greater are present in solution in proportions varying continuously with concentration and temperature. On the other hand, it is extremely unlikely that when a substance like hydrogen gas dissolves in water a chemical combination of any kind takes place.

freezing point. It may be stated in words thus: The "relative" diminution in the escaping tendency of the solvent upon the addition of an infinitesimal amount of a solute is equal to the ratio of the number of gram molecules of solute and solvent. It is probable that equation (12 b), besides being more general than the equation of Raoult, is also more accurate; for it will appear likely from the theory here developed that Raoult's law is exact only when the vapor of the solvent follows the gas law, but that equation (12 b) represents a universal law.

Our problem is now to show that equations (11) and (12) are directly deducible from the idea of thermal pressure contained in equation (10). Since the reasoning would be the same whether our goal is the general equation (12) or the special form of Raoult, for the sake of concreteness it will be convenient to develop first the latter equation, and in the simple case of a solution in a solvent to whose vapor the gas law may be applied. Let us determine theoretically in this case the influence of the solute on the vapor pressure of the solvent. This effect may be divided into two which are entirely independent; the first is the effect of the thermal pressure of the solute on the condition of the solvent (this may be pictured kinetically as the influence of the mere motion of the solute molecules); the second is the effect of the attraction or repulsion of the solute for the particles of the solvent. It will therefore simplify the discussion if we study these two influences separately, beginning with the latter.

In a hypothetical case in which we may imagine the particles of the solute to be evenly distributed through a solution, and to have no effect except by an attraction for the solvent particles, the only practical effect of the presence of the solute will be to increase the attractive pressure of the solvent inward. Then, in order to maintain equilibrium, according to equation (4),

$$P = \beta - a,$$

since the external pressure is unchanged, the total volume will decrease on account of the new attraction until the thermal pressure of the solvent is increased by the same amount as the attractive pressure, and we may write, therefore,

$$d\beta = da; \quad \text{or,} \quad d\beta - da = 0.$$

Comparing this with equation (5) or equation (7), it is evident that *the attraction of solute for solvent is not the cause of the lowering of vapor pressure in a solution*, and that a mere attraction or repulsion between the solvent and solute does not change the vapor pressure of the solvent,

because the change in the attractive pressure is always compensated by an equal change in the thermal pressure, and these two changes produce equal and opposite effects upon the vapor pressure. This conclusion will simplify the discussion of the second influence of the solute, the effect of thermal pressure; for since the attraction or repulsion of solute for solvent is without effect, we may consider with perfect generality the case in which this attraction or repulsion is zero. In such a case, if β and a represent the thermal and attractive pressures of the pure solvent, when the solute is added in general a change in volume occurs in which β and a change to $\beta + d\beta$ and $a + da$. The total attractive pressure of the solution is $a + da$; but the total thermal pressure of the solution includes the partial thermal pressure of the solute, which may be designated by $d\beta'$. The equation of the solution is, then,

$$P = (\beta + d\beta + d\beta') - (a + da). \tag{13}$$

Combining this with the equation of the pure solvent,

$$P = \beta - a,$$

we obtain

$$d\beta - da = -d\beta'. \tag{14}$$

Now the vapor pressure depends on the attractive pressure and the thermal pressure of the solvent alone, in accordance with equation (7), which may be written,

$$\frac{dP_1}{P_1} = \frac{d(\beta - a)}{\frac{mRT}{V}}.$$

Substituting equation (14) and writing from equation (10),

$$d\beta' = \frac{(dn)\ RT}{V},$$

we obtain,

$$\frac{dP_1}{P_1} = -\frac{\frac{(dn)\ RT}{V}}{\frac{mRT}{V}} = -\frac{dn}{m},$$

dP_1 being negative for a decrease in P_1. This is a statement of the law of Raoult, which is thus shown to be a direct consequence of the principle of thermal pressure expressed in equation (10). Perhaps a more intimate understanding of the way in which the thermal pressure of the solute affects the vapor pressure of the solvent may be obtained from another point of view which affords a simple but somewhat less rigorous demonstration.

In any pure solvent, according to equation (5), the tendency to escape into some other phase is dependent, not upon the actual values of the thermal and attractive pressures, but only upon their difference, which is the external pressure. At constant external pressure, therefore, the escaping tendency of the solvent is constant under all circumstances as long as the external pressure represents the difference between the thermal pressure of the solvent and the attractive pressure. If in a solution the thermal pressure of the solvent were equal to the total thermal pressure, the difference between this and the attractive pressure would be equal to the external pressure, and the escaping tendency would be the same as that of the pure solvent under the same external pressure. In reality the total thermal pressure is the sum of the partial thermal pressures of the solvent and solute; therefore, other things being equal, the escaping tendency should be to that of the pure solvent as the partial thermal pressure of the solvent is to the total thermal pressure. That is,

$$\frac{\psi_2}{\psi_1} = \frac{\beta}{\beta + \beta'},$$

where β is the partial thermal pressure of the solvent, β' that of the solute; but from equation (10),

$$\beta' = \frac{n R T}{V}; \quad \beta = \frac{m R T}{V}$$

therefore,

$$\frac{\psi_2}{\psi_1} = \frac{m}{m + n}.$$

From this equation,

$$\frac{\psi_1 - \psi_2}{\psi_1} = \frac{n}{m + n},$$

which is equation (12 a).

From this it appears that the lowering of vapor pressure, the lowering of solubility, and the lowering of the freezing point are all due to the fact that the solute shares with the solvent the support of the external and attractive pressure. Other things being equal, the greater the thermal pressure of the solute the less that of the solvent, and thus an increase in the amount of the solute diminishes the escaping tendency of the solvent, whether towards the gaseous phase, the solid phase, or another liquid.

An analogy may illustrate this explanation of Raoult's law, and at the same time introduce the consideration of osmotic pressure. If we consider m gram molecules of a gas A under a constant external pressure,

its tendency to escape is measured by that pressure. If n gram molecules of another gas B are now introduced, while the external pressure remains constant, the partial pressure of A is diminished by the fraction $\frac{n}{m+n}$ of its original value, and its escaping tendency will be diminished in the same ratio. Therefore gaseous solutions also obey equation (12), and in this case the explanation is obviously the one which has been given here for solutions in general.

If now we imagine the external pressure to be produced by the gas A outside, while within the pressure is borne by A and B, and if we imagine the outside and inside connected by a membrane permeable to A alone, then the gas A having a lower partial pressure inside will pass in from the outside, and equilibrium will not be established until the partial pressure of A is the same inside and outside; that is, until the total pressure inside is greater than that outside by the partial pressure of B. This is an exact analogy to the osmotic pressure in solutions, and in fact the same explanation can be given for both.*

Let us consider a solution and the pure solvent at the same external pressure originally, connected by a semipermeable membrane. The tendency to pass from solution to solvent is less than the tendency to pass from the solvent to solution, as we have seen. The solvent will therefore flow into the solution until, in some way, this tendency is balanced. Let us suppose that it is balanced by an increase in the external pressure on the solution. Then, since the function ψ of the solvent has been decreased by the thermal pressure of the solute, according to equation (14) it must be restored to its original value by an external pressure equal to that thermal pressure. In other words, the osmotic pressure of a dilute solution must be equal to the partial thermal pressure of the solute and,

$$\Pi = \frac{n R T}{V},$$

which is the law of van 't Hoff. This may be shown mathematically as follows: —

By generalizing equation (13) we obtain, as the equation of the solution, when the external pressure upon the solution is variable,

$$P + dP = \beta + d\beta + d\beta' - \alpha - d\alpha. \qquad (15)$$

* Since this paper was written an exactly similar statement of this analogy between the osmotic pressure and the pressure which a mixture of gases would show under the above conditions has been given by Ikeda, Zeit. Phys. Chem., XXXII. 280 (1900).

For the solvent,

$$P = \beta - a.$$

Combining these we obtain,

$$dP = d\beta - da + d\beta'.$$

For equilibrium, when the escaping tendencies of the solution and solvent are the same,

$$d\beta - da = 0.$$

Hence the equation for osmotic equilibrium is,

$$dP = d\beta'.$$

But $dP = d\Pi$, the osmotic pressure, and

$$d\beta' = \frac{(dn)\,R\,T}{V},$$

from equation (10); hence

$$d\Pi = \frac{(dn)\,R\,T}{V},$$

the equation of van 't Hoff.

The conclusion that a certain osmotic pressure, and an equal change in the external pressure, together have no effect upon the tendency of a solvent to escape into some other phase may be verified in an interesting way.

In Figure 4 let A represent a pure liquid X; B, a solution in X, whose osmotic pressure is Π; C, the vapor of X; and D, an inert, insoluble gas exerting a pressure equal to Π. M and M′ are two membranes permeable to X alone. Since the gas pressure in D is equal to the osmotic pressure Π, X will not pass through the membrane M, therefore none of X will distil from solution to solvent or *vice versa*, for such a distillation would form a cyclic process contradicting the second law of thermodynamics. Hence the vapor pressure over a solution is the same as that over the pure solvent when the solution has an additional external pressure applied, equal to its osmotic pressure. The effect of the thermal pressure of a solute upon the vapor pressure of a solvent may be regarded, therefore, as due to a stress upon the surface of the solution acting like a diminution in external pressure of the same magnitude.

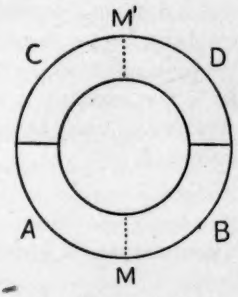

FIGURE 4.

IV.

If further investigation and further accordance with observed facts prove that the principle of thermal pressure, which has been here shown to possess a high degree of probability, is in fact an exact and universal law of nature, then there are few physico-chemical phenomena in which thermal pressure is not one of the most important determining factors; yet it would be premature to attempt at present any general application of the new theory. But there is one field in which the view here advocated is in direct conflict with a well-known and fruitful theory, — the theory of van der Waals. We shall, therefore, consider briefly the relations of thermal pressure to the equation of condition of liquids and gases and the van der Waals formula.

Equations (4) and (10) give at once a general equation of condition for all substances,

$$P = \frac{n R T}{V} - a, \quad \text{or} \quad P = \frac{R T}{v} - a, \tag{16}$$

where n is the total number of gram molecules in the volume V, and a, the attractive pressure, is the only quantity which is not immediately determined. It is probably, in most cases, a complicated function of volume and also of temperature.

Equation (16) is directly opposed to the theory of van der Waals, in that it does not recognize the influence upon the pressure of the so-called covolume, but, on the other hand, it in no way contradicts the validity of the equation of van der Waals considered as a purely empirical formula; for if that equation is regarded merely as a statement of experimental observation, it may be written as well in some other form. For example, instead of

$$P = \frac{R T}{v - b} - \frac{a}{v^2},$$

the second term might be expanded, and the equation written,

$$P = \frac{R T}{v} + R T \left(\frac{b}{v^2} + \frac{b^2}{v^3} + \frac{b^3}{v^4} \cdots \right) - \frac{a}{v^2}.$$

It would then be in the form of equation (16), in which

$$a = R T \left(\frac{b}{v^2} + \frac{b^2}{v^3} + \frac{b^3}{v^4} \cdots \right) - \frac{a}{v^2}.$$

This form of a would be of significance only in case the equation of van der Waals were perfectly accurate; as a matter of fact, no one has

claimed for it absolute accuracy, and it is probable that, except for its plausible theoretical basis, it would already have given place to a more accurate, purely empirical equation. If equation (16) is used in place of the formula of van der Waals as the equation of condition of gases and liquids, then the form of the function a must be found for each substance separately from its empirical equation; and on account of the presence of this function of unknown form, it is obviously impossible at present to test by experiment the validity of equation (16).

The curve of attractive pressure may be easily plotted in diagram on the PV plane. On this plane the rectangular hyperbola which, in the older theory, is only of ideal significance as the limit towards which the equation of condition tends as the substance approximates the perfect gas, in our present theory always represents a real physical quantity, — the thermal pressure. If from the ordinates of this hyperbola are subtracted the ordinates of the actual equation of condition, then, according to equation (4), these differences may be drawn as ordinates of the curve of attractive pressure. A general survey of many such curves will be necessary in order to show what general laws govern the variation of the quantity a. This task must be reserved for the future, but it may be confidently predicted that interesting and useful relations will be found which will give to equation (16) a specific value which it now lacks on account of its great generality; for the study of coincident conditions shows that from the behavior of one unassociated liquid or gas we may predict the behavior of any other, and therefore it seems eminently probable from equation (16) that since β has the same form for all substances, the form of the substance a for any simple liquid or gas will be found to be closely related to its form for any other simple liquid or gas.

Notwithstanding the indefiniteness given to equation (16) by our ignorance concerning the quantity a, in one respect the equation is explicit, and is again in direct antagonism to the equation of van der Waals. It follows directly from our equation that the pressure of any substance is greater than, equal to, or less than the corresponding pressure of a perfect gas, according as the attractive pressure is less than, equal to, or greater than zero. In other words, whenever the volume of any phase is greater than the volume that it would occupy as a perfect gas, a is negative, and the total resultant force between the molecules must be repulsive. Regarding such a repulsion, which finds no place in van der Waals' theory, it is true that there is little positive evidence, but what evidence there is seems to indicate decidedly the existence in some cases of some kind of a repulsive force. If a liquid is cooled at constant pressure, its

volume does not appear to tend to become zero at the zero of temperature, but rather to approach as a limit some definite volume. As the kinetic forces become less there must be some other force which enters to oppose the attraction between the molecules. If it is permissible to consider the limiting case where the motion of the molecules ceases, there must exist at the absolute zero a condition in which the total external pressure and all the attractive forces between the molecules are together balanced by some sort of outward force which is equal to their sum. This would be greater than the attractive forces alone, and the difference would depend upon the external pressure. In other words, there would be a resultant repulsive force equal to the external pressure. As to whether this force is of the nature of elasticity, or of some action at a distance, it would be presumptuous to speculate. From these considerations, which must be admitted to be very hypothetical, it would seem that at ordinary temperatures there should be analogous conditions in which the repulsive forces would be greater the higher the pressure. According to equation (16), in all liquids the resultant attractive pressure diminishes with increasing external pressure, and finally changes sign at the point where on the PV diagram the equation of condition cuts the hyperbola of thermal pressure; that is, at the point where the volume is the same as it would be if the substance were to behave as a perfect gas under the same pressure. Similarly, at high pressures probably all gases have a greater volume than corresponds to the gas law, and according to our theory their particles repel each other under these conditions. At atmospheric pressure, on the other hand, almost all gases have too small a volume, but hydrogen still has a volume which corresponds in our theory to an intermolecular repulsion. It is interesting, therefore, to note that in the experiments of Joule and Thomson, while other gases showed an increase of internal energy on expansion, hydrogen showed a slight decrease. Helium is in all probability another gas which has too great a volume; and it has been shown by Donnan * from his experiments on the effusion of gases, that probably helium also has a heating effect on free expansion, like hydrogen. Such a heating effect can be explained in no other way so simply as by assuming that there is a repulsion between the molecules in both helium and hydrogen. Finally, a similar repulsion could explain the phenomenon observed in the experiments of Ramsay † on the distribution of hydrogen between two spaces, one of which contained hydrogen alone, the other hydrogen and nitrogen. He

* Phil. Mag., XLIX. 423 (1900). † Phil. Mag., XXXVIII. 206 (1894).

found that, if the two spaces were connected by a semipermeable membrane, the partial pressure of the hydrogen was less in the space containing nitrogen. This could be easily explained by assuming a repulsion between a molecule of hydrogen and one of nitrogen, and this explanation is again in full accord with the observation of Joule and Thomson that hydrogen mixed with nitrogen greatly decreased the cooling effect of the latter when expanding through a porous plug. These bits of evidence, accumulated, point decidedly to the truth of equation (16).

It was stated above that in general a is a function of the temperature; for if either in equation (16) or in the equation of van der Waals the term representing intermolecular attraction should be independent of the temperature, it would follow immediately from thermodynamics that the specific heat at constant volume of a liquid or a vapor should be independent of its volume, and also that a liquid and its vapor should have the same specific heat at constant volume.* All our evidence, both experimental † and theoretical,‡ is opposed to this conclusion. There is little doubt that the specific heat at constant volume, even in gases, changes in all cases, and sometimes considerably, with an isothermal change in volume; and it may be noted that while the equation of van der Waals is incompatible with any deviation in the specific heat at constant volume, such a deviation is a direct consequence of our present theory. For, since the specific heat depends upon the energy required to raise a substance from one temperature to another, and since that energy, according to any kinetic theory, is partly consumed in increasing the kinetic energy of the molecules, the specific heat must depend in part upon the kinetic energy of the molecules at the two temperatures. According to the accepted kinetic theory the energy of progression of the molecules must be the same at any one temperature under all conditions. The energy required to increase the progressive energy of the molecules from one temperature to another would depend, therefore, on the two temperatures, and would be independent of all other circumstances. On the other hand, according to the views expressed on page 154, the kinetic energy of the molecules may vary at any temperature according to the other conditions of a substance. Let us consider a gas in which there is no attractive or repulsive force between the molecules. According to the theory hitherto accepted, if the volume occupied by the

* Cf. Nernst, Theor. Chem., p. 234 (1898).

† Joly, Phil. Trans. Roy. Soc., 182 A, 73; Proc. Roy. Soc., XLVII. 218; LV. 390.

‡ Lewis, These Proceedings, XXXV. 1 (1899); Zeit. Phys. Chem., XXXII. 364 (1900).

molecules * of the gas were appreciable, then the progressive energy of the molecules would be the same as if it were a perfect gas, but the pressure would be greater than the pressure of a perfect gas. According to our new theory the pressure in this case would be necessarily the same as that of a perfect gas, and therefore the kinetic energy of the molecules must be less than that of the molecules of a perfect gas. In general, then, we should expect the internal kinetic energy to diminish with the volume.

This is an important consequence of the new theory, and it is evident that the volume of the molecules must be as important in our theory as in that of van der Waals; but in the former the quantity "b" concerns energy relations, while in the latter it concerns pressure relations. We are thus led to a consideration of the total change in internal energy in an isothermal change of volume of a liquid or a gas, and in the change from a liquid to a vapor.

It has frequently been assumed that the energy change in such a process is a measure of the attractive forces which oppose or assist the process. In an earlier paper † I have shown that this is the case only when the specific heat at constant volume remains the same; and, in fact, it is obvious that the change in potential energy which is a measure of attraction is in general only one factor of the total change in energy which includes also any change in the internal energy of the molecules as well as the change in progressive energy of the molecules, which is assumed in our present theory.

These three factors will be designated as follows: The change in potential energy, or Free Energy, which is the measure of intermolecular attraction, will be represented by dX; change in the progressive motion of the molecules by dE; change in the internal energy of the molecules by dI. If dU is the total change in internal energy,

$$dU = dX + dE + dI. \tag{17}$$

In the paper ‡ already referred to I have developed the general thermodynamic equation of condition,

$$P = \frac{RT}{v} - F(v)\,T - \frac{dU}{dv} + T\int_{T_0}^{T} \frac{1}{T}\frac{dc_v}{dv}\,dT, \tag{18}$$

* This phrase is used in conformity to usage. The quantity "b" of van der Waals may be defined more generally and less hypothetically as a quantity depending on the difference between the time in which two molecules approach, collide, and separate, and the time which two mathematical particles would require for the same process.

† Lewis, l. c. ‡ Ibid.

where $F(v)$ is an unknown function of v, and c_v is the molecular heat at constant volume, T_0 some arbitrary temperature. Comparing this with equation (16), we obtain

$$a = F(v)\,T + \frac{dU}{dv} - T\int_{T_0}^{T} \frac{1}{T}\frac{dc_v}{dv}\,dT. \tag{19}$$

Now, substituting dU from (17), and bearing in mind that $a = \frac{dX}{dv}$, we obtain

$$\frac{dE}{dv} + \frac{dI}{dv} = T\int_{T_0}^{T} \frac{1}{T}\frac{dc_v}{dv}\,dT - F(v)\,T. \tag{20}$$

This is the closest insight that we can obtain at present into the general form of $\frac{dE}{dv} + \frac{dI}{dv}$, but it is sufficient to show that in general the total change in energy is not identical with the change in potential energy, at least when $\frac{dc_v}{dv}$ is not zero.

If we could pass continuously from the liquid to the gaseous state, and equation (16) were assumed to hold good continuously throughout the process, the total work of the process could be found, and would be equal to the actual work done in the evaporation of the liquid. From equation (16),

$$\int p\,dv = \int \frac{RT}{v}\,dv - \int a\,dv,$$

or

$$\int_{v_1}^{v_2} p\,dv = RT\ln\frac{v_1}{v_2} - \int_{v_1}^{v_2} a\,dv;$$

or, since $a = \frac{dX}{dv}$, the total work is

$$RT\ln\frac{v_1}{v_2} - \int_{v_1}^{v_2} dX.$$

The work done in evaporation at the same temperature is $P'(v_1 - v_2)$, where P' is the vapor pressure. We may write, therefore,

$$P'(v_1 - v_2) = RT\ln\frac{v_1}{v_2} - \int_{v_1}^{v_2} dX.$$

Now, if dX were always equal to dU, we could write

$$RT\ln\frac{v_1}{v_2} = (U_1 - U_2) + P'(v_1 - v_2) = L, \tag{21}$$

where L is the common heat of evaporation.

Now, as a matter of fact, $RT\ln\frac{v_1}{v_2}$ is always less than L, and this is precisely what would be predicted from our theory; for in passing from a liquid to a vapor energy must be used not only in overcoming the intermolecular attraction $\left(\text{the quantity that would be equal to } RT\ln\frac{v_1}{v_2}\right)$, but also in providing for the increase in the progressive energy of the molecules, which was shown on page 165 to be a necessary consequence of our theory.

In concluding this brief treatment of some of the consequences of our theory, we may mention one that is important in the study of homogeneous equilibrium. The isothermal, according to our present view, is not identical with the line of constant internal energy of progression of the molecules, which might also be called the line of constant molecular velocity; the latter line must, therefore, be of considerable independent importance; for if we regard the mass law kinetically as an expression of the law of probability, the chance of any two molecules reacting must depend upon their momentum at impact, and this would be constant along the line of constant molecular velocity, and not along the isothermal. The mass law, then, disregarding other disturbing factors, should hold along the former line rather than the latter. On account of an entire lack of data that would give any experimental evidence on this point, this mere suggestion of a possible future modification in the theory of chemical kinetics must suffice.